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Journal of Organometallic Chemistry 486 (1995) 109–114

Journal of Organometallic Chemistry

Chemistry of coordinatively unsaturated and electron deficient carbonyl metallate ions. Gas phase reactions of $[Fe(CO)_2]^-$ with alcohols

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Received 6 April 1994

Abstract

The gas phase reactions of the metal dicarbonyl anion $Fe(CO)_2^-$ with fifteen isotopically unlabelled, D- and ^{13}C-labelled C_{2-6} alcohols have been studied by the use of Fourier transform ion cyclotron resonance mass spectroscopy. Several competitive reaction channels which are related to the structures of the alcohols as well as their carbon content have been identified for these systems. For the primary alcohols, separate decarbonylation and dehydrogenation channels along with a channel involving C–H and O–H bond activations to give $Fe(CO)_3^-$ as an end product have been identified. With C_{3-6} primary alcohols the predominant terminal reaction product is one which involved *bis*-dehydrogenation of a collision complex. For secondary alcohols, no $Fe(CO)_3^-$ product ions were detected and the dominant reaction channel was one which resulted in *bis*-dehydrogenation of a collision complex. With tertiary alcohols, ROH, the major ionic and dehydrogenated product was of the type $[(CO)_2Fe(OR-H)]^-$.

Keywords: Iron; Ion cyclotron resonance; Mass spectroscopy; Carbonyl; Metal carbonyl anions; Ion/molecule reactions

1. Introduction

Electron deficient and coordinatively unsaturated carbonyl metallate ions $[Metal(CO)_x]^-$ are now well recognized reactive species in the condensed phase [1,2] and are increasingly being shown to undergo a diversity of reactions with molecular substrates in the gas phase [3–9]. New advances in this area of experimental gas phase ion chemistry have been made possible recently by the applications of Fourier transform ion cyclotron resonance (FTICR) [10–15] and flowing afterglow (FA) [16,17] spectroscopic techniques. The advantages as well as the limitations of these instrumental methods for the study of solvent-free ion/molecule reactions in the gas phase have been the subjects of recent detailed reviews [10,13,15,17].

Recently there has been some qualitative support for the view that electron deficiency coupled with coordinative unsaturation at the metal centre is responsible for the reactions of metal carbonyl anions with molecular substrates. It is now established, for example, that the 14- and 13-electron ions $Mn(CO)_3^-$ and $Fe(CO)_2^-$ react, by insertions into C–H bonds with dimethyl ether [18], methanol [9,19], alkanes [9,21], cycloalkanes [20,21], and alkenes [7,22]. Less common insertions into C–C bonds have been identified for the reactions of the 13-electron ion $Cr(CO)_3^-$ with aliphatic aldehydes, ketones and esters [23]. Drift cell ICR measurements have shown that $Cr(CO)_3^-$, $Fe(CO)_3^-$, $Co(CO)_2^-$ and $Co(CO)(NO)^-$ activate both C–H and O–H bonds in their respective reactions with alcohols [24], while flowing afterglow experiments have demonstrated that the ion $HCr(CO)_3^-$ activates O–H bonds in both alcohols and water [25]. The O–H bond activation in water and methanol has been identified with the cationic species $[Fe(CH_3)]^+$ in a recent trapped ion study [26]. Moreover, the 16-electron species $V(CO)_5^-$ also has been shown to dehydrogenate methanol via an initial oxidative insertion into to a C–H bond, but is unreactive towards C_2–C_4 alcohols because of steric constraints in a reaction intermediate [27].

More recently we have been involved in a comprehensive trapped ion/molecule study of the reactions of

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SSDI 0022-328X(94)05038-D

the 13-electron ion Fe(CO)_2^- with methanol and five of its isotopomers, specifically CD_3OH, CH_3OD, CD_3OD, $^{13}\text{CH}_3\text{OH}$ and $\text{CH}_3^{18}\text{OH}$, in order to examine in detail the mechanisms of C–H and O–H bond activations and associated bond insertions by the metal centre. Three discrete and competitive reaction channels have been revealed for these seemingly simple systems as a result of using the isotopically labelled methanols [28]. Thus, for unlabelled methanol, three primary reaction products have been identified: $[\text{HFe(CO)(OCH}_3)]^-$, formed in a decarbonylation channel; Fe(CO)_3^-, formed in a channel involving both C–H and O–H bond activation and *bis*-dehydrogenation of a collision complex; and $[(\text{CH}_2\text{O})\text{Fe(CO)}_2]^-$, formed in a separate channel involving the elimination of a single H_2 molecule [28]. An additional and significant secondary reaction has also been identified in which the primary product ion $[\text{HFe(CO)(OCH}_3)]^-$ reacts further with methanol to give the *bis*-alkoxy-substituted metal carbonyl ion $[(\text{CH}_3\text{O})_2\text{Fe(CO)}]^-$ at trapping times of several seconds [28]. As part of a continuing study of gas phase metal carbonyl anion chemistry [5–8,22,23,28], and in order to gain new insights into activations of C–H and O–H bonds by reactive metal centres, we have examined in detail the trapped-ion/molecule reactions of the 13-electron linear ion $[\text{Fe(CO)}_2]^-$ [29,30] with a representative series of fifteen unlabelled and isotopically labelled primary, secondary, tertiary and cyclic C_2–C_6 alcohols, and the results are presented below.

2. Experimental section

All ion/molecule experiments were performed in a Bruker Spectrospin CMS-47 FTICR spectrometer. Details of this instrument, its associated operational procedures and the experimental techniques employed for examining ion/molecule reactions have been fully described [10,13,15].

Table 1
Alcohols used in reaction with $[\text{Fe(CO)}_2]^-$

Alcohol	Isomer	
I	C_2H_5OH	ethanol
II	$\text{CH}_3{}^{13}\text{CH}_2\text{OH}$	ethyl-1-^{13}C alcohol
III	$\text{CH}_3\text{CD}_2\text{OH}$	ethyl-1,1-d_2 alcohol
IV	C_2H_5OD	ethan(ol-d)
V	n-C_3H_7OH	1-propanol
VI	i-C_3H_7OH	2-propanol
VII	i-C_3H_7OD	2-propanol(ol-d)
VIII	n-C_4H_9OH	1-butanol
IX	i-C_4H_9OH	2-methyl-1-propanol
X	s-C_4H_9OH	2-butanol
XI	t-C_4H_9OH	2-methyl-2-propanol
XII	t-C_4H_9OD	2-methyl-2-propanol(ol-d)
XIII	n-$C_5H_{11}OH$	1-pentanol
XIV	n-$C_6H_{13}OH$	1-hexanol
XV	c-$C_6H_{11}OH$	cyclohexanol

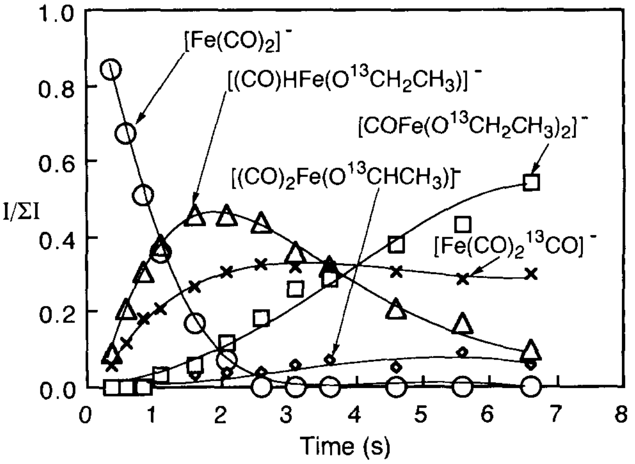


Fig. 1. Variations of ion abundances with time for the reaction of $[\text{Fe(CO)}_2]^-$ with ethyl-1-^{13}C alcohol (**II**). $I/\Sigma I$ = ion abundance/sum of ion abundances. ^{56}Fe considered.

Iron pentacarbonyl, Fe(CO)_5, as the neutral precursor of Fe(CO)_2^-, was admitted along with all the volatile alcohols to the ICR cell through a 40°C temperature regulated inlet system via individual Balzers precision leak valves type BDV-035. The ICR cell temperature was somewhat above ambient, ca. 35°C. Electron ionization (5eV) of Fe(CO)_5 at a pressure of 5×10^{-8} mbar gave the ionic products Fe(CO)_x^- with $x = 1 - 4$, as previously described [7], from which Fe(CO)_2^- was mass selected to react with the relevant alcohol after the admission of the alcohol to the ICR cell to give a total pressure of 2.5×10^{-7} mbar. Indicated pressures were measured with a Balzers IMR-132 ionization gauge positioned ca. 10 cm above the Balzers TPU-330 turbomolecular pump [7]. Details of the relevant pulse/delay sequences employed in the various ion/molecule experiments have been given previously [5–8].

Iron pentacarbonyl was obtained from Strem Chemicals Inc and the alcohols were high purity samples from Aldrich, Fluka and BDH. These were admitted to the inlet system of the FTICR spectrometer after being subjected to multiple freeze–pump–thaw cycles to remove non-condensables. The isotopically labelled alcohols were obtained from Cambridge Isotope Laboratories and Sigma-Aldrich. Isotopic purities and specfic alcohol sample purities were routinely checked from low voltage positive ion mass spectra obtained with the CMS-47 FTICR instrument.

3. Results and discussion

The fifteen C_2–C_6 alcohols whose reactions with Fe(CO)_2^- were examined are listed in Table 1, while

Tables 2–5 identify the ionic reaction products and their abundances for all the $Fe(CO)_2^-/C_{2-6}$ alcohol systems at times (2 s) when the reaction of $Fe(CO)_2^-$ was complete. Representative plots of the variations with time of ionic product distributions ('time-plots'), Figs. 1–4, illustrate and identify the principal ion/molecule processes and ion decomposition pathways for the $Fe(CO)_2^-/C_{2-6}$-alcohol reaction series and thereby contribute to mechanistic interpretations of the results.

Three primary ionic products have been identified from the reactions of (**I**)–(**IV**) with $Fe(CO)_2^-$, Table 2, namely $[(CO)(H)Fe(OR)]^-$ a decarbonylated product formulated as an hydrido complex [25]; $Fe(CO)_3^-$, a rearrangement product arising from CH_4 and H_2 eliminations from a collision complex, and a dehydrogenated ionic product $[(CO)_2Fe(OR\text{-}H)]^-$. A secondary ionic product, $[(CO)Fe(OR)_2]^-$ was formed at longer trapping times (seconds) from the reaction of $[(CO)HFe(OR)]^-$ with the alcohol ROH which was

Table 2
Ionic product distributions for reactions of C_2-alcohols with $[Fe(CO)_2]^{-a}$

Alcohol	ROH	Ionic reaction products (%)			
R		$[(CO)(H)Fe(OR)]^-$	$[(CO)Fe(OR)_2]^-$	$[Fe(CO)_3]^-$	$[(CO)_2Fe(OR\text{-}H)]^-$
$CH_3 \cdot CH_2$	(**I**)	15	43	28	14
$CH_3 \cdot {}^{13}CH_2$	(**II**)	46	13	32 [b]	5
$CH_3 \cdot CD_2$	(**III**)	43	21	28	7 [c]
$CH_3 \cdot CH_2$ [d]	(**IV**)	11 [e]	24	40	25

[a] Reaction delays of 2 s and $[Fe(CO)_2]^- = 0$ (completely reacted) unless otherwise indicated.
[b] $[Fe(CO)_2(^{13}CO)]^-$; also (unreacted) $[Fe(CO)_2]^- = 5\%$.
[c] $[(CO)_2Fe(OCDCH_3)]^-$.
[d] **IV** = CH_3CH_2OD.
[e] $[(CO)(D)Fe(OC_2H_5)]^-$.

Table 3
Ionic product distributions for reactions of C_3-alcohols with $[Fe(CO)_2]^{-a}$

Alcohol	ROH	Ionic reaction products (%)					
R		$[(CO)(H)Fe(OR)]^-$	$[(CO)Fe(OR)_2]^-$	$[Fe(CO)_3]^-$	$[(CO)_2Fe(OR\text{-}H)]^-$	$[(CO)Fe(OR\text{-}H)]^-$	$[(CO)_2Fe(OR\text{-}H\text{-}H_2)]^-$
n-C_3H_7	(V)	2	5	10	0	0	82
i-C_3H_7 [b]	(VI)	8	13	0	8	10	60
i-C_3H_7 [c]	(VII)	11 [d]	5	0	5	11	65

[a] Reaction delays of 2 s and with $[Fe(CO)_2]^- = 0$ (completely reacted).
[b] Reaction delay = 1.7 s.
[c] **VII** = i-C_3H_7OD.
[d] $[(CO)(D)Fe(OC_3H_7)]^-$.

Table 4
Ionic product distributions for reactions of C_4-alcohols with $[Fe(CO)_2]^{-a}$

Alcohol	ROH	Ionic reaction products (%)						
R		$[(CO)(H)Fe(OR)]^-$	$[(CO)Fe(OR)_2]^-$	$[(Fe(OR)_2]^-$	$[Fe(CO)_3]^-$	$[(CO)_2Fe(OR\text{-}H)]^-$	$[(CO)Fe(OR\text{-}H)]^-$	$[(CO)_2Fe(OR\text{-}H\text{-}H_2)]^-$
n-C_4H_9	(**VIII**)	0	5	0	8	5	0	82
i-C_4H_9	(**IX**)	0	8	8	8	0	0	77
s-C_4H_9	(**X**)	5	1	1	0	0	2	91
t-C_4H_9	(**XI**)	23	14	0	0	63	0	0
t-C_4H_9 [b]	(**XII**)	15 [c]	1	0	0	85	0	0

[a] Reaction delays of 2 s and with $[Fe(CO)_2]^- = 0$ (completely reacted).
[b] **XII** = C_4H_9OD.
[c] $[(CO)(D)Fe(OC_4H_9)]^-$.

Table 5
Ionic product distributions for reactions of C_5- and C_6-alcohols with $[Fe(CO)_2]^{-a}$

Alcohol	ROH	Ionic reaction products (%) [b]						
R		$[(CO)Fe(OR)_2]^-$	$[(CO)Fe(OR)]^-$	$[Fe(OR)_2]^-$	$[Fe(CO)_3]^-$	$[(CO)_2Fe(OR\text{-}H)]^-$	$[(CO)_2Fe(OR\text{-}H\text{-}H_2)]^-$	$[(CO)Fe(OR\text{-}H\text{-}H_2)]^{-c}$
n-C_5H_{11}	(**XIII**)	3	0	6	11	0	71	8
n-C_6H_{13} [d]	(**XIV**)	3	0	7	10	0	63	17
c-C_6H_{11}	(**XV**)	0	14	0	0	7	80	0

[a] Reaction delays of 2 s and with $[Fe(CO)_2]^- = 0$ (completely reacted), unless otherwise indicated.
[b] Ionic products corresponding to *mono*-decarbonylated collision complexes viz., $[(CO)(H)Fe(OR)]^-$ were not detected in this series.
[c] Only the *bis*-dehydrogenated and *mono*-decarbonylated ion was detected; ions of formulation $[(CO)Fe(OR\text{-}H)]^-$ were not detected.
[d] Reaction delay 1.5 s.

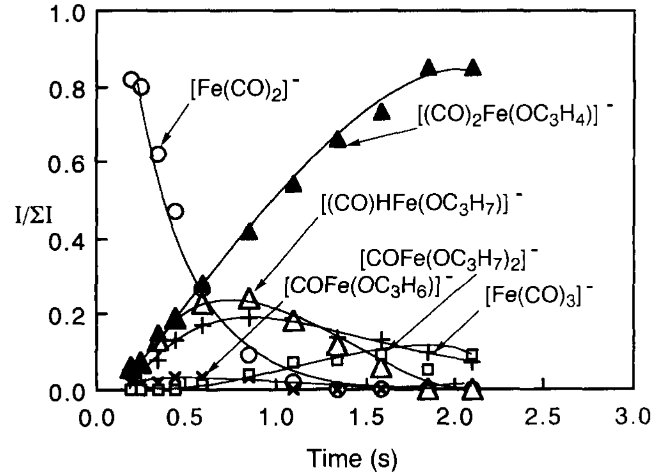


Fig. 2. Variations of ion abundances with time for the reaction of $[Fe(CO)_2]^-$ with 1-propanol (V). $I/\Sigma I$ = ion abundance/sum of ion abundances. ^{56}Fe considered.

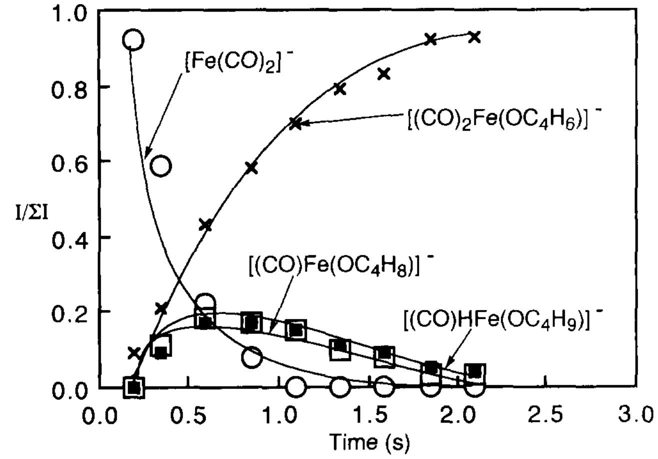


Fig. 3. Variations of ion abundances with time for the reaction of $[Fe(CO)_2]^-$ with 2-butanol (X). $I/\Sigma I$ = ion abundance/sum of ion abundances. ^{56}Fe considered.

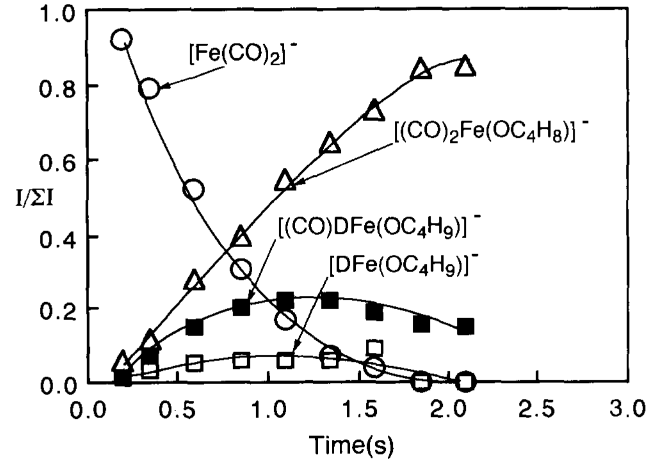
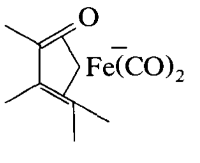


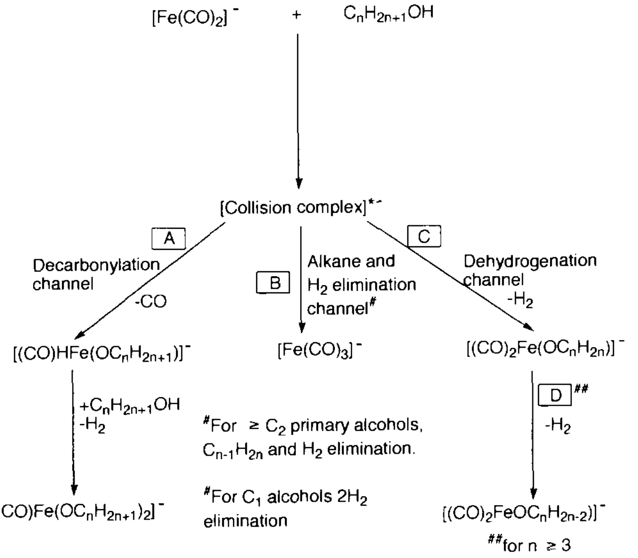
Fig. 4. Variations of ion abundances with time for the reaction of $[Fe(CO)_2]^-$ with 2-methyl-2-propan(ol-d) (XII). $I/\Sigma I$ = ion abundance/sum of ion abundances. ^{56}Fe considered. Low abundances ca. 1% of $[(CO)Fe(OC_4H_9)_2]^-$ were also detected at 2 s trapping times.

present in excess. Formation of this secondary product may be rationalized in terms of an insertion of the metal centre into the O–H alcohol bond, along with the elimination of H_2 from an unstable dihydrido intermediate; that is, in the reaction $[(CO)HFe(OR)]^- + ROH \rightarrow [(CO)Fe(OR)_2]^- + H_2$. Use of the ^{13}C labelled alcohol $CH_3^{13}CH_2OH$, Fig. 1, gave results consistent with the time resolved data and conclusions for the reaction of I with $Fe(CO)_2^-$, vide supra, and further confirmed that the α-carbon site of metal centre is involved in the insertion into the alcohol, since only the ion with *m/z* 141, viz. $[Fe(CO)_2(^{13}CO)]^-$, was detected, and no ionic product at *m/z* 140. Concomitant alkane (CH_4) and dihydrogen elimination from a collision complex may thus be proposed for this particular reaction channel. It is noteworthy that alkane eliminations have been identified previously in trapped ion reactions of aldehydes with the 13-electron ion $Cr(CO)_3^-$, which led, in one reaction channel, to the formation of the tetracarbonyl anion $Cr(CO)_4^-$ [23]. The identity of the dehydrogenated product formed in a separate reaction channel for the present C_2-alcohol/$Fe(CO)_2^-$ systems was further confirmed by the use of (III) CH_3CD_2OH (III) which yielded the primary product ion $[(CO)_2Fe(OCDCH_3)]^-$, and at longer ion trapping times (2–3.5 s) the ionic product $[(CO)Fe(OCD_2CH_3)_2]^-$, which comes from the secondary $[(CO)HFe(OCD_2CH_3)]^-/CH_3CD_2OH$ reaction (see Table 2).

For *n*-C_3H_7OH (**V**) (Table 3), and the other primary alcohols (**VIII**) and (**IX**), (Table 4), and (**XIII**) and (**XIV**) (Table 5) reaction and ion decomposition channels similar to those for the C_2 alcohols can be defined. These channels, which are respectively labelled A, B and C, are summarized in Scheme 1. However, in the case of these C_3–C_6 primary alcohols viz., (**V**), (**VIII**), (**IX**), (**XIII**), (**XIV**) the most abundant ionic product was identified as a *bis*-dehydrogenated species $[(CO)_2Fe(OR{-}H{-}H_2)]^-$ (Fig. 2), a *bis*-dehydrogenated [$Fe(CO)_2^-$/alcohol] adduct. We suggest that this ionic product is formed as a consequence of hydrogen atom migrations from the β- and γ-carbon atoms of a mono-dehydrogenated-alcohol/$Fe(CO)_2^-$ precursor to the metal centre to give an unstable intermediate that undergoes a further H_2 elimination to give an η^4-unsaturated aldehyde ligand species bonded to $Fe(CO)_2^-$, **XVI** (Scheme 1, channel D). In an earlier drift cell ICR study of the reactions of the 13-electron ion $Cr(CO)_3^-$ with C_3–C_6 alcohols a comparable *bis*-dehydrogenation channel was identified [24].



XVI



Scheme 1.

Another consistent ionic product from the reactions of the C_3–C_6 primary alcohols with $Fe(CO)_2^-$ is $Fe(CO)_3^-$ which, as previously noted for the $Fe(CO)_2^-$/methanol system [28], is the product of a reaction channel involving oxidative activation of both C–H and O–H bonds and *bis*-dehydrogenation of a collision complex.

The secondary alcohols **(VI)**, **(VII)**, **(X)** and **(XV)** reacted differently with $Fe(CO)_2^-$ (Tables 3–5 and Fig. 3). Significantly no $Fe(CO)_3^-$ product ions were detected, presumably due to the non-availability of two α-C atom hydrogens to migrate from the alcohol to the metal centre and allow the elimination of the corresponding alkane and H_2, Scheme 1, Channel B. The preferred reaction channel in all these cases was that which resulted in *bis*-dehydrogenation from the collision complex shown in Scheme 1, Channels C and D, and which is exemplified by the time-plot for the 2-butanol/$Fe(CO)_2^-$ system given in Fig. 3. The terminal product ion in this case is an η^4-unsaturated ketone ligand-$Fe(CO)_2^-$ species, bonded similarly to **XVI**, and also similarly to ionic products previously identified as arising by dehydrogenation of ketone-$Cr(CO)_3^-$ systems [23].

As with the secondary alcohols, and for complementary reasons to those given above, the tertiary and cyclic alcohols **(XI)**, **(XII)** and **(XV)** do not react with $Fe(CO)_2^-$ via alkane and H_2 eliminations to form $Fe(CO)_3^-$ product ions. Fig. 4 presents a typical time resolved data plot for these systems; namely that for the $(CH_3)_3COD/Fe(CO)_2^-$ reaction. Apart from *mono*- and *bis*-decarbonylated product ions, the principal product for this system was the *mono*-dehydrogenated species. Isotopic labelling revealed that these ions arise as a consequence of H_2 (or HD) elimination from a *bis*-hydrido (or HD) intermediate formed by metal centre insertion into the O–H (or O–D) alcohol bond and H-migration from an alcohol β-carbon atom to the metal centre.

In conclusion, a further diversity of reactions which include C–H and O–H bond activations, metal centre oxidative insertions, dehydrogenation alkane eliminations and decarbonylation processes, depending on the structure of the alcohol, have been identified in the reactions of this C_{2-6} alcohol series with the 13-electron coordinatively unsaturated $Fe(CO)_2^-$ ion. The principal aim of this study has been realized with the definition of the several competitive reaction channels (Scheme 1) involved in the trapped-ion/molecule study of the fifteen $Fe(CO)_2^-$/alcohol systems.

Acknowledgement

Support of this work by the Australian Research Council is acknowledged.

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